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Patentanmeldung Nr.	Patent application No.	Demande de brevet n°

03075948.4

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The possibilities of electrowinning AL from AL2S3

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The Possibilities of Electrowinning Al from Al$_2$S$_3$

5   Primary aluminum production via the Hall-Héroult process consumes about 13-15 MWh of electrical energy per tonne of aluminum. The anodes are consumed during the electrowinning process and have to be changed periodically. In addition, the Hall-Héroult process gives rise to green house emissions such as CF$_4$ and C$_2$F$_6$, which are usually removed from the off-gas in compliance with environmental legislation. In 10 the alternative sulfide process, sulfur is produced at graphite anodes without consuming those. The fluoride off-gases as well as spent pot linings will not be produced, since the electrolyte is basically composed of chlorides. The sulfide intermediate, Al$_2$S$_3$, is produced by the reaction of CS$_2$ and alumina. The flowsheet of the proposed Compact Aluminum Production Process (CAPP^{TM}), for which a patent application has been filed, is discussed in a paper by Xiao et al. The contents of the application WO/00/37691, 1999 15 is deemed to be included in this description by this reference. If Al$_2$S$_3$ can successfully be produced, i.e. if the process is technically feasible and cost effective, the aluminum metal can be extracted by electrolysis, producing sulfur gas at the anode. The sulfur gas will be recycled to produce CS$_2$, which is used in the sulfidation step, which is of particular advantage in combination with the CAPP-process. The simplified reactions (assuming no 20 complex ions) of the electrolysis process are:
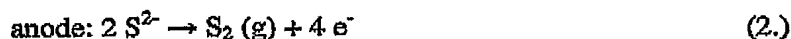
$$\text{cathode: } Al^{3+} + 3e^- \rightarrow Al \tag{1.}$$

$$\text{anode: } 2\,S^{2-} \rightarrow S_2\,(g) + 4\,e^- \tag{2.}$$

$$\text{Overall: } Al_2S_3 \rightarrow 2\,Al + 1.5\,S_2\,(g) \tag{3.}$$

Figure 1 shows immediately that the electrolysis of Al$_2$S$_3$ is very promising with regard to energy consumption, i.e. it has the lowest decomposition potential. Note that the first bar is a theoretical value for comparison to the cloride and sulfide route, and the third bar represents the actual Hall-Héroult process. The theoretical value of the 25 decomposition potential is determined by:

$$E^0 = -\frac{\Delta G^0}{nF} \tag{4.}$$

The alkali chloride electrolyte permits a relatively low operating temperature of about 700 °C, or just above the melting point of aluminum. Because of operation with non-consumable anodes, the interelectrode gap can be reduced and a multi-polar cell operation is possible, which will increase productivity, reduce energy consumption and 30 reduce capital costs. As Al$_2$S$_3$ reacts with air and water, operation under an inert atmosphere is preferred.
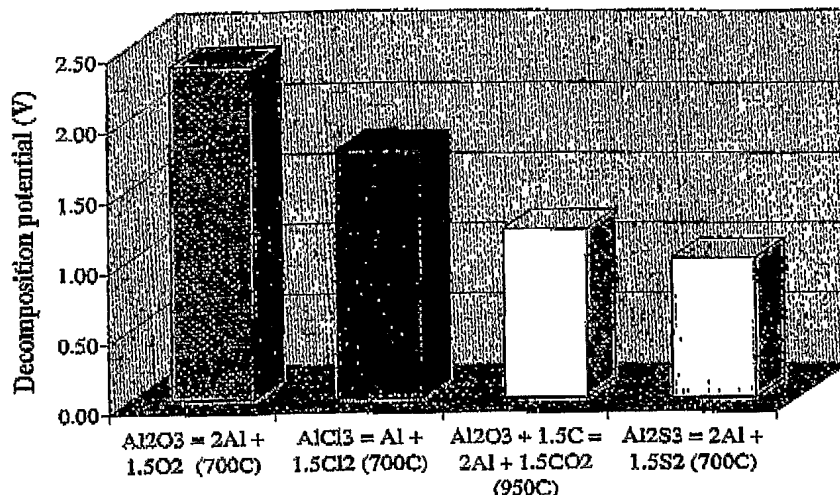
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Figure 1 - Decomposition potential of aluminum species to produce aluminum by electrowinning

5   The eutectic of a $MgCl_2$-NaCl-KCl mixture (50-30-20 mole%) has been considered previously as an appropriate electrolyte for the electrolysis of Al_2S_3. The solubility of Al_2S_3 in this melt was found to be ~3 wt.% at 750 °C. The solubility of Al_2S_3 is enhanced by $MgCl_2$ according to the reaction:

$$MgCl_2 + Al_2S_3 \rightarrow 2\ AlSCl + MgS\ (s) \tag{5.}$$

10   The addition of $AlCl_3$ results in a more acidic melt, but due to the high vapour pressure of $AlCl_3$ (boiling point = 447 °C), additions are limited, because of volatilization. The addition of 5-10 wt.% $AlCl_3$ increases the solubility of Al_2S_3 up to a maximum of 5-7 wt.% according to the following reaction:
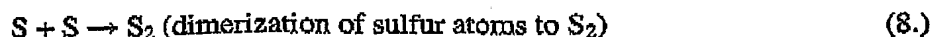
$$AlCl_3 + Al_2S_3 \rightarrow 3\ AlSCl \tag{6.}$$
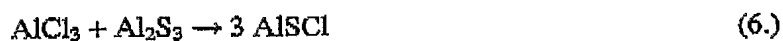
     Raman spectroscopic studies indicated the presence of a series of chainlike
15   $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ with $n \geq 3$ and polymeric $[AlSCl_2]_n^{n-1}$ (for large n) at temperatures around 400 °C. It is reasonable to assume that the structure will break down at the temperatures employed for electrowinning, i.e. > 700 °C; thus, it is likely that AlSCl will be present in the melt.

     Electrochemical studies of Al_2S_3 in a chloride melt showed that the reduction of
20   Al-ions at a graphite electrode is a diffusion controlled process and proceeds via a reversible, 3-electron charge transfer. The oxidation of S-ions in the chloride electrolyte is a reversible diffusion controlled process proceeding via a mechanism based on two steps:

3

$$S^{2-} \rightarrow S + 2e^- \text{ (electrochemical 2-electron process)} \qquad (7.)$$

$$S + S \rightarrow S_2 \text{ (dimerization of sulfur atoms to } S_2) \qquad (8.)$$

The diffusion coefficients of Al (D_{Al}) and S (D_S) are listed in Table I, indicating that the current density is cathodically limited. In a fluoride melt D_S is of the same order of magnitude as is D_S in a chloride eutectic melt. Since the aluminum and sulfide ions are likely to exist as complexes (e.g. AlS^+), the actual calculated diffusion coefficients of
5   sulfur would increase. The Al_2S_3 concentration listed as wt.% has been calculated assuming an electrolyte density of $1.6 \cdot 10^3$ kg·m^{-3} (Table II).

Table I - Apparent Diffusion Coefficients of Al and S Ions in Molten Salt Electrolytes

Electrolyte	Temp (K)	Al_2S_3 (mol%)	Al_2S_3 (wt.%)	D_{Al} (cm² s⁻¹)	D_S (cm² s⁻¹)	Ref.
MgCl$_2$-NaCl-KCl eut.	750	$8.47 \cdot 10^{-6}$	$7.5 \cdot 10^{-2}$	$5.4 \cdot 10^{-6}$	$2.59 \cdot 10^{-5}$	
MgCl$_2$-NaCl-KCl eut. + AlCl$_3$	750	$8.47 \cdot 10^{-6}$	$7.5 \cdot 10^{-2}$	$1.03 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	
LiF-NaF eut.	750	$6.61 \cdot 10^{-6}$	$5.8 \cdot 10^{-2}$	–	$1.47 \cdot 10^{-5}$	
Na$_3$AlF$_6$	1050	$1.3 \cdot 10^{-5}$	$1.1 \cdot 10^{-1}$	–	$3.95 \cdot 10^{-5}$	

Minh et al. reported a limiting current density of 0.3 A·cm^{-2} at the saturation solubility of Al_2S_3 (~3 wt.%) and 0.2 A·cm^{-2} in the MgCl$_2$-NaCl-KCl eutectic containing
10   2 wt.% Al_2S_3. The current efficiency was determined to be about 80% at a current density of 0.2 A·cm^{-2}, a cell potential of about 1.5 V and interelectrode gap of 3 cm. Adding 10 wt.% AlCl$_3$ to increase the solubility of Al_2S_3 up to 5 wt.% and to increase the concentration of Al-ions, current densities of up to 2 A·cm^{-2} can be reached. Then, the current density is limited by the anodic reaction.

15   There is not much information available on the physical properties of a MgCl$_2$-NaCl-KCl melt of 50-30-20 mole%. However, Table II shows the physical properties of two binary melts to give an indication of the physical properties. In addition, the properties of a cryolite-alumina melt are given for comparison to the Hall-Héroult process. The density of a chloride melt is lower than for cryolite, facilitating easy
20   separation of aluminum from the electrolyte. The surface tension and viscosity of ternary eutectic melt are estimated to be respectively about 40% and 50% lower than for the cryolite-alumina melt, which is also beneficial to the electrowinning operation.

Table II - Properties of Chloride Mixtures and of a Cryolite-Alumina Mixture

Species	Comp. (mol%)	T_m (°C)	κ (S cm⁻¹)	D (mm² s⁻¹)	ρ (g cm⁻³)	η (10⁻³ N s m⁻²)	γ (10⁻³ N m⁻¹)
MgCl$_2$-NaCl-KCl (at 750 °C)	50-30-20	385	no data	0.79	no data	no data	no data
MgCl$_2$-NaCl (at 750 °C)	60-40	600	1.9	0.45*	1.7	1.4	82
MgCl$_2$-KCl (at 750 °C)	60-40	510	1.3	0.15*	1.6	1.3	77
Na$_3$AlF$_6$-Al$_2$O$_3$ (at 1000 °C)	90-10	960	2.5	2.8*	2.1	2.7	132

* extrapolated from measurement range

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EXPERIMENTAL

The electrowinning of aluminum from aluminum sulfide is carried out in a two electrode system. A schematic view of the experimental cell is depicted in Figure 2. The cathode is a pool of molten aluminum (effective area 8.1 cm^2), which is polarized by a
5   graphite block connected by a rod of stainless steel shielded by a quartz tube. The anode is constructed of a graphite block of 1 cm^2, 5 cm high, which is immersed 2 cm into the electrolyte and is connected by a stainless steel rod . The interelectrode gap is 2 cm. The anode acts as the reference electrode, thus the cell potential is measured during the electrolysis. The electrochemical cell is constructed of sintered Al_2O_3 (Alsint). The melt
10   is protected by an inert Ar atmosphere. The cell is externally heated by a 2100W cylindrical furnace equipped with heating elements. The maximum operating temperature is 1400 °C. The temperature is measured and controlled by type S thermocouples and a control unit. The furnace has water-cooled flanges.

The potential is measured with a PGSTAT30 potentiostat/galvanostat, which was
15   used in combination with a BSTR20A current booster, to enable a high current throughput (20 A range). The electrochemical measurement system is fully computer controlled.
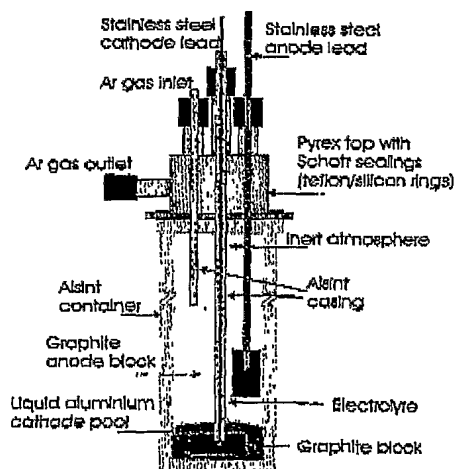

Figure 2 – Schematic view of the experimental electrowinning cell

20

All chemicals were stored and handled in a glove box, having an argon atmosphere (< 1 ppm H_2O, O_2). KCl, NaCl and NaF were of pro analysis quality. Anhydrous $MgCl_2$ (98%), Al_2S_3 (98%) and Na_3AlF_6 (98%) were commercially obtained from a supplier. The chloride electrolyte mixture was composed and put in a container in
25   the glove box. This container was then taken out of the glove box and heated to 450 °C while purging HCl gas through the solids and subsequently through the melt to remove all water and oxides. After cooling the container was put back into the glove box. The

Al_2S_3 and fluxes were added at room temperature in the glove box. The electrowinning cell was assembled in the glove box, closed, then transported to the furnace where an Ar flow prevented contact with air. An overview of the salt mixtures used for the experimental program discussed in this paper is given in Table III.

Table III – Overview of Experimental Program of the
Electrowinning of Al from Al_2S_3 in a $MgCl_2$-NaCl-KCl
Electrolyte of 50-30-20 mole% at 725 °C.

Exp.	Al_2S_3 (wt.%)	Flux	Amount of flux (wt.%)
A	4	--	--
B	4	-	-
C	4	Na_3AlF_6	10
D	10	Na_3AlF_6	10
E	4	Na_3AlF_6	5
F	4	Na_3AlF_6	15
G	4	Na_3AlF_6	20
H	4	Na_3AlF_6	30
K	4	NaF	10
L	4	NaF	30

RESULTS

Electrolysis of Al_2S_3 in the $MgCl_2$-NaCl-KCl Eutectic

Figure 3 shows the results of the electrolysis of Al_2S_3 with the ternary eutectic at an operating temperature of 725 °C. This temperature makes this eutectic electrolyte in particular suitable for combinations with the CAPP-process. Excess Al_2S_3 has been added to the melt to ensure a solution which is saturated with Al_2S_3 (maximum = 3 wt.%). Experiments A and B are duplicate experiments and it is shown that reproducibility is good. The off-set of the reaction has been determined by extrapolation of the j-E relationship to the intercept with the x-axis. The apparent decomposition potential is $E = -1.1$ V, which is close to the theoretical value of -0.98 V at 725 °C. It can be determined from the Nernst equation (9.) that this is caused by an activity lower than 1:

$$E = E^0 + \frac{RT}{nF}\ln\frac{a(Al^{3+})}{a(Al)} \qquad (9.)$$

The limiting current density is about 0.2 A·cm^{-2}, which is in agreement with the results of Minh et al. However, assuming that maximum solubility of Al_2S_3 in the eutectic melt was obtained, the limiting current density of 0.3 A·cm^{-2}, which they

6

reported, was not reached. Possibly, some of the Al_2S_3 reacted with air or moisture, resulting in a lower apparent concentration.
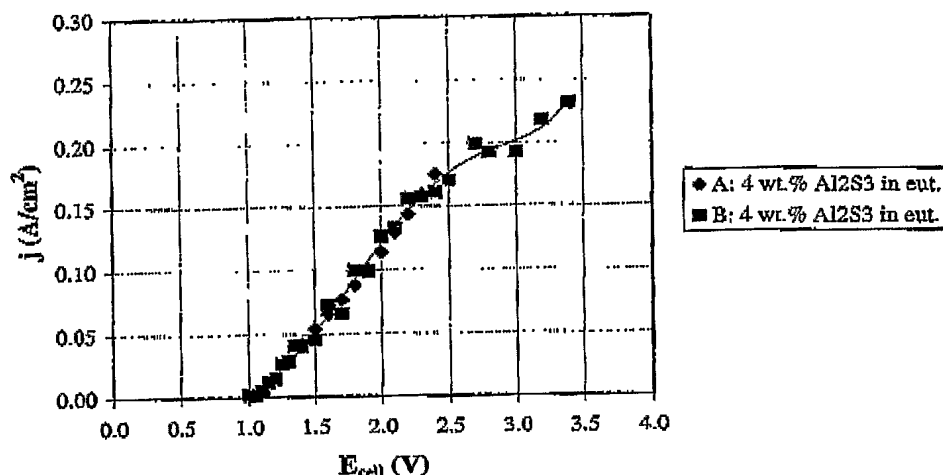

Figure 3 - Cathodic current density as a function of the cell potential for the electrowinning of Al from Al_2S_3 in a MgCl$_2$-NaCl-KCl electrolyte of 50-30-20 mole% at 725 °C. Reproducibility test.

The Influence of Cryolite as a Flux

The limiting current densities found are too low to compete with the Hall-Héroult process, where about 0.8 A·cm^{-2} is employed. Therefore, the addition of fluxes to the melt was considered to increase the solubility of Al_2S_3 and to increase the activity of both Al and S in the melt. Minh et al. used AlCl$_3$ to enhance the electrowinning process. Since AlCl$_3$ is readily volatilized from the melt and has to be separated from sulfur downstream to recycle it to the electrowinning process, it was discarded as being impractical.

It was decided to investigate the effect of cryolite, since it has a much higher melting point ($T_m = 1012$ °C) and volatilization at the cell operating temperature of 700-750 °C is assumed to be negligible. In addition, it is assumed that it can influence the AlSCl complexes in the electrolyte, or form different complexes, e.g. AlF$_n^{x-}$ in accordance with the anion complexes reacting at the cathode in a cryolite melt.

It can be argued that adding fluoride is not desirable, since this results in fluoride emissions. However, the required amount of cryolite is relatively small and operating temperatures are only about 700 °C, thus the vapor pressure of fluorides will be very low. The anode effect can be avoided, because sulfur reacts at the anode. As non-consumable anodes can be used, the electrowinning can be carried out in a closed system, providing improved off-gas capturing.

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Figure 4 shows a major improvement of the electrowinning performance, because of the addition of Na_3AlF_6. When adding 10 wt.% of Na_3AlF_6, the electrolyte composition changes to a quaternary mixture of 48-29-19-4 mole% of $MgCl_2$-NaCl-KCl-Na_3AlF_6. The current density is more than 3 times larger at a given cell potential. By
5   linear extrapolation it has been determined that $E = 0.98$ V, which equals the theoretical decomposition potential. The Nernst equation (9.) indicates that the activity of Al_2S_3 in a melt with cryolite addition approaches unity. Further increase of the Al_2S_3 concentration in the melt did not produce a significant effect (compare experiments C and D). Figure 5 depicts a graph showing the influence of the amount of cryolite added to the melt. There
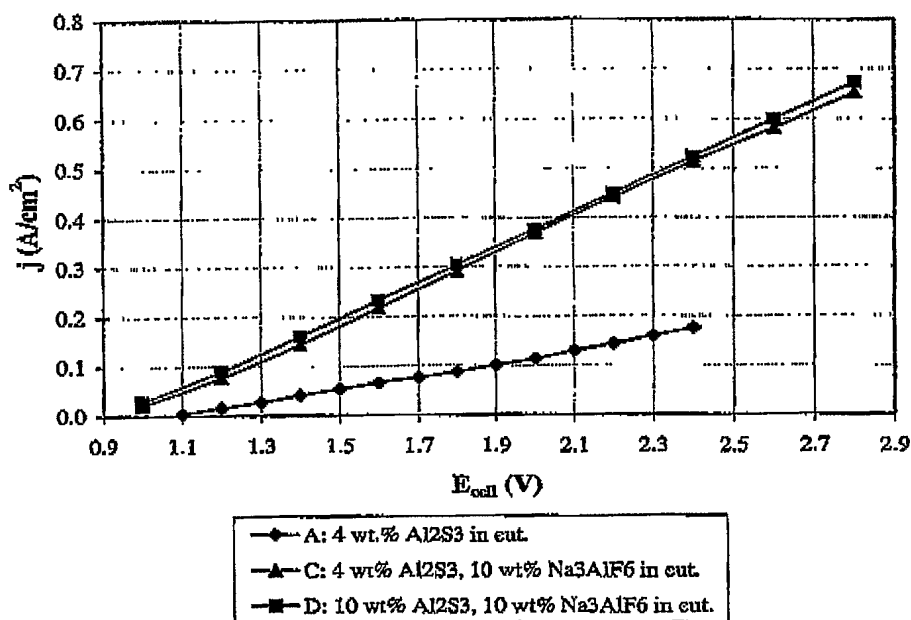10   seems to be an optimum at about 10 wt.% cryolite addition.

Figure 4 - Plot of cathodic current density as a function of the cell potential for the electrowinning of Al from Al_2S_3 in a $MgCl_2$-NaCl-KCl electrolyte of 50-30-20 mole% at 725 °C, using cryolite as a flux
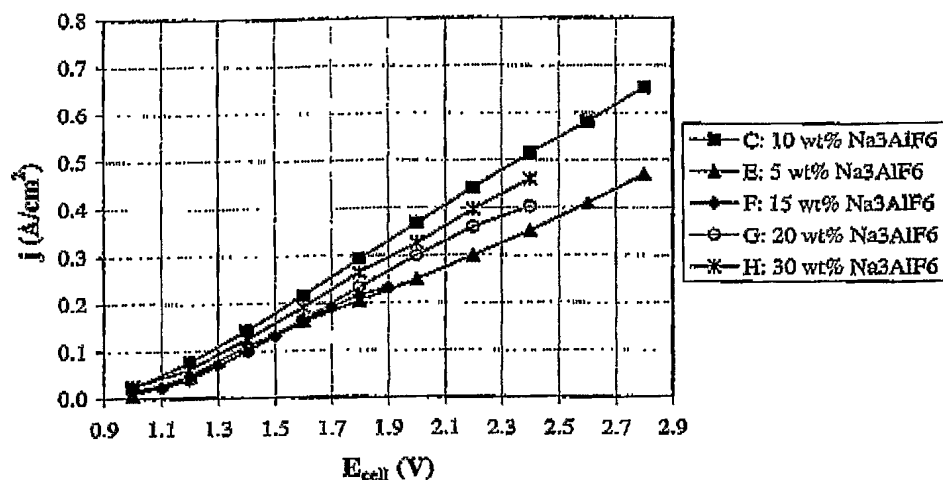
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Figure 5 - Plot of cathodic current density as a function of the cell potential for the electrowinning of Al from 4 wt.% Al_2S_3 in a $MgCl_2$-NaCl-KCl electrolyte of 50-30-20 mole% at 725 °C, using different amounts of cryolite as a flux

The Influence of NaF as a Flux

Experimental work has been carried out in order to investigate whether the positive influence of cryolite on the performance of the electrowinning was caused by the amount fluoride added, or by increasing the amount of Al-ions in the electrolyte. Therefore, NaF was used as a fluxing agent. The addition of 10 wt.% NaF results in a melt composition of 42-25-17-16 mole% $MgCl_2$-NaCl-KCl-NaF composition. On an elemental basis, the amount of F in the electrolyte is comparable to the cryolite melt, i.e. 6.4 and 7.6 mole% F respectively. Figure 6 depicts the results of those experiments. Increasing the amount of NaF to 30 wt.% shows a deteriorating cell performance, which again is in agreement with the results of cryolite additions.
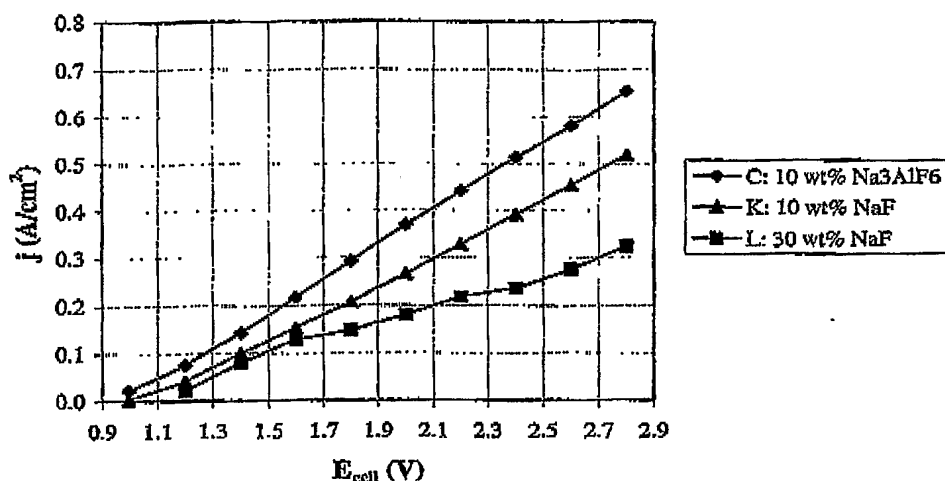
Figure 6 - Cathodic current density as a function of the cell potential for the electrowinning of Al from 4 wt.% Al_2S_3 in a $MgCl_2$-NaCl-KCl electrolyte of 50-30-20 mole% at 725 °C, using NaF as a flux

5

DISCUSSION

The cell potential consists of thermodynamic, kinetic (activation potential and mass transfer limitations) and ohmic contributions, which have been expressed by Leistra
10 and Sides for electrolysis involving gas evolution. The linear j-E relationships observed from Figure 4 to Figure 6 indicate that the electrowinning process with these high concentrations of dissolved Al_2S_3 (compared to Table I) is no longer diffusion controlled, but shows ohmic limitations. Then, an increased solubility of Al_2S_3 would not result in a substantial enhancement of the cell performance. This is supported by the experimental
15 results. It is assumed that the addition of Na_3AlF_6 to the melt has a positive effect on the solubility of Al_2S_3. Therefore, the amount of Al_2S_3 added to the quaternary mixture was increased from 4% to 10% (Exp. C and D in Figure 4). However, this did not improve the cell performance significantly, indicating that diffusion is not the rate limiting step with these relatively high concentrations of Al_2S_3 employed.

20 At first sight, it can be argued that because of the ohmic control of the process, increasing the conductivity of the melt should result in an increased current density. Since cryolite has a higher conductivity than the chloride eutectic (Table II), a better performance is at least to some extent the result of the increased conductivity. When adding 10 wt.% of Na_3AlF_6, the electrolyte composition changes to a quaternary mixture
25 of 48-29-19-4 mole% of $MgCl_2$-NaCl-KCl-Na_3AlF_6, which can have significantly different properties. However, the slope of the linear relationship increased by almost a

factor 3 when cryolite was added, which cannot be attributed to the increased conductivity of the melt only. Furthermore, although the specific conductivity of NaF is the highest of all components, i.e. $4.2 \ \Omega^{-1} \cdot cm^{-1}$ at 725 °C, the effect of adding NaF is less pronounced.

5   As cryolite and NaF additions produce similar effects, it can be argued that the amount of fluoride contributes to the positive effect on the electrowinning process, resulting from a higher activity of AlF_n^{m-} than AlS^+ species. Also, when complexing of Al with F is favored over complexing with S, the concentration of S-ions is higher when fluoride is added, favoring the anodic reaction. The molar ratio of F:Al for the experiments with 4 wt.% Al_2S_3 and additions of 10 wt.% Na_3AlF_6, 10 wt.% NaF and 30

10   wt.% NaF are 2.7, 4.1 and 10.3 respectively. Regarding Figure 6, the molar ratio of F:Al seems to be a parameter to control the j-E characteristics of the electrowinning process.

In summary, the following observations have been made that justify the conclusion that the benefical effect of the addition of fluoride containing fluxes cannot solely be ascribed to the increased specific conductivity of the melt:

15   • The slope of the j-E relationship increases by almost a factor 3 on the addition of cryolite to the $MgCl_2$-NaCl-KCl eutectic, i.e. much more than can be expected from the increased conductivity.
     • The addition of 10 wt.% Na_3AlF_6 shows a larger improvement of the apparent conductivity than the addition of NaF, although the specific conductivity of NaF is
20   much higher.
     • There seems to be an optimum amount of fluoride, or fluoride to aluminum ratio, in the electrolyte.

25   The explanation proposed is that a significant portion of the ohmic drop is not related to the melt itself but due to the gas bubbles at the anode, since they have virtually zero conductivity and reduce the available anode surface. Minh et al. showed that the main contribution to the cell potential is due to the anodic reaction. It has been determined previously for chlorine evolution in a chloride melt that the apparent conductivity was only about 40% of the specific conductivity of the electrolyte, due to

30   gas bubbles. Chlorine bubbles have the tendency to grow and stick to the anode and the overpotential could be interpreted as an ohmic potential drop in a surface layer at the anode. The same reasoning may apply as regards the evolution of sulfur gas in a chloride melt.

Therefore, a hypothesis can be postulated that on the addition of fluoride, a

35   complex ion is formed, changing interfacial tension at the anode, resulting in different characteristics of the sulfuric bubble layer at the anode surface area, significantly reducing the ohmic drop as well as the energy consumption. Further research is in progress to understand these phenomena completely.

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CONCLUSIONS

Electrowinning of Al from Al_2S_3 is technically feasible. Small additions of cryolite are preferred to achieve sufficient current densities. The energy consumption can be reduced significantly, while realizing a current density that can compete with the Hall-
5   Héroult process. In addition, the proposed electrowinning process features non-consumable anodes, no CO_2 emissions and a minimization of fluoride emissions.

CLAIMS

1. A process for the electrolysis of Al_2S_3, using a molten salt, preferably a chloride melt wherein additives are made to the melt to improve the electrical conductivity so as to increase the current density.

2. A process according to claim 1, wherein the additives comprise a fluoride.

3. A process according to claim 2, wherein the fluoride comprises cryolite.

4. A process according to claim 3, wherein the concentration of the cryolite is in the range of 5-20%, preferably 7-13%.

5. A process for the electrolysis of Al_2S_3, wherein measures are taken to reduce the amount and/or size of gas bubbles formed at the anode of the electrolysis cell.

6. A process according to claim 5, wherein the measures comprise adding a fluoride to the molten salt in which the electrolysis is carried out.

7. A process to claim 6, wherein the fluoride comprises cryolite.

8. A process according to claim 7, wherein the concentration of cryolite is in the range of 5-20%, preferably 7-13%.

9. A process according to any of the preceding claims, wherein the electrolysis cell is a multi-polar cell.

10. A process according to any of the preceding claims, wherein the Al_2S_3 is made in a process as described in patent application WO 00/37691, 1999.

ABSTRACT

The objective of this research is to investigate an alternative process for the production of primary aluminum via a sulfide intermediate. By the proposed route it is
5   expected that the electrical energy consumption can be reduced by almost 60%. Aluminum will be produced from Al_2S_3 by electrowinning, creating sulfur gas at the anode, which can be recycled within the process. The results of an experimental investigation into the possibilities of Al_2S_3 electrolysis in a molten chloride electrolyte, a 50-30-20 mole% $MgCl_2$-$NaCl$-KCl mixture, are discussed. It is shown that electrolysis of
10   Al_2S_3 is technically feasible.

PCT/EP2004/003625